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APPARATUS FOR GAS-ANALYSIS LABORATORIES AT COAL MINES

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CONTENTS.

Page.
Introduction — 5
  Dangerous underground gases — 5
Occurrence of methane — 6
  Safety-lamp indications — 6
  Gas-analysis indications — 7
Collection of samples — 8
Sampling gases to verify safety-lamp indications — 10
Apparatus for exact determination of methane and carbon dioxide — 10
  Method of using apparatus — 11
Apparatus for exact determination of methane — 14
Portable apparatus for determination of methane — 15
Portable apparatus for determination of carbon dioxide and methane — 17
Modified Orsat apparatus for complete approximate analysis of mine air — 18
Preparation of solutions—details of apparatus — 21
  Caustic potash solution — 22
  Alkaline pyrogallate solution — 22
  Cuprous chloride solution — 22
  Apparatus required — 22
Publications on mine accidents and methods of mining — 24

ILLUSTRATIONS.

FIGURE 1. Hand pump and container for taking samples of mine gases — 8
2. Rack for sampling tubes — 9
3. Laboratory form of apparatus for the exact determination of carbon dioxide and methane — 11
4. Laboratory form of apparatus for the exact determination of methane — 14
5. Portable apparatus for the determination of methane — 15
6. Portable apparatus for the determination of carbon dioxide and methane — 18
7. Modified Orsat apparatus for the complete analysis of mine air — 19

APPARATUS FOR GAS-ANALYSIS LABORATORIES AT COAL MINES.

By GEORGE A. BURRELL and FRANK M. SEIBERT.

INTRODUCTION.

In the course of its investigations relating to mine fires and explosions, the Bureau of Mines has been carefully studying the composition of mine atmospheres and the most efficient methods of detecting those mine gases that are dangerous. Some results of that study are presented in this paper, which is published as one of a series of reports dealing with problems of mine ventilation.

The coal-mining laws of various States limit the number of men that may work on each air current, state the minimum quantity of air allowed per man per minute, and require that sufficient air shall be forced underground to dilute, render harmless, and carry from the mine all smoke, foul air, and noxious and explosive gases. In other words, these State laws recognize that the proper introduction of fresh air is the best means of removing dangers due to underground gases.

DANGEROUS UNDERGROUND GASES.

Dangerous underground gases include those that exert a poisonous or depressing effect on the human system and those that form inflammable or explosive mixtures with air.

In the air of properly ventilated mines operating under normal everyday methods, such an excess of carbon dioxide or such a deficiency of oxygen as would in itself cause harm is seldom encountered. However, at the working faces of some mines and in old workings there may be a deficiency of oxygen and an excess of carbon dioxide, as compared with normal mine air, that will prevent lamps from burning and be prejudicial to health. In addition, powder smoke may linger and the air may be so warm and moist that bad effects will be experienced by the miners.

Harmful proportions of carbon monoxide, hydrogen sulphide, and oxides of nitrogen are rarely present in mine air except at working faces where explosives have been fired. At working faces, however, as mentioned above, extremely harmful proportions of gases produced by blasting explosives are liable to be present for some time after a blast. Large quantities of carbon monoxide and carbon diox-

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ide are then often produced; hydrogen sulphide also is sometimes formed. Oxides of nitrogen result from the improper detonation of certain classes of explosives. Immediately after a shot there may escape from the crevices produced by the blast both carbon monoxide and hydrogen so mixed with methane liberated from the coal as to make the mixture extremely inflammable. Carbon monoxide in deadly quantities is also formed by mine explosions and fires. Hydrogen, too, is produced under such conditions.

OCCURRENCE OF METHANE.

Methane is found in all parts of many coal mines. It may accumulate in large quantities in still atmospheres, especially in the goave, at working faces, or in cavities in the roof, but it is given off in other places, and its detection and estimation constitute one of the necessary precautions in obtaining good mine ventilation.

As a result of the better understanding of the part fire damp plays in colliery disasters, chemical analysis of the air in different parts of a mine is being given more consideration by colliery officials.

Methane is the constituent of mine atmospheres that coal-mine officials usually desire to have determined as accurately as possible. Frequently the carbon-dioxide content of the air is desired, or an apparatus is desired for the determination of carbon dioxide, carbon monoxide, hydrogen, methane, and nitrogen. The object in assembling specially designed apparatus for this work was to provide simple, easily manipulated types that would be sufficiently accurate for the use proposed.

Because of the part methane has played in local gas explosions in mines, and because of the liability of such explosions to initiate disastrous dust explosions, many collieries are extremely vigilant in their efforts to prevent accumulations of methane. At a few mines [a] in this country chemical analyses of the atmosphere in the returns are frequently made in order to detect any increase in the volume of methane escaping from the coal. Abroad the practice has been followed at some mines for years.

The methods that one American coal-mining company uses for determining carbon monoxide are those of Hesse,[b] and for methane those of Winkler.[c]

SAFETY-LAMP INDICATIONS.

Most mining companies depend upon the safety lamp exclusively for discovering the presence of fire damp. With the safety lamp a quantity of methane likely to quickly become dangerous can be detected by the appearance of a cap on the flame of the lamp. With some lamps a proportion of methane as low as 2 per cent can be detected; skilled observers having good eyesight may detect as little as 1.5 per cent or less. Special lamps, not by any means in common use, will detect even less, but with none of them can small percentages of methane be determined as accurately as by chemical analysis.

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[a] The methods employed by the Consolidated Coal Co., West Virginia, are described by J. G. Smyth, Gas in mine-air currents: West Virginia Coal Min. Inst., 1909, pp. 66 and 83.

[b] Hempel, Walther, Methods of gas analysis, translation 3rd German ed., by L. M. Dennis, 1910, p. 337.

[c] Winkler, Clemens, Handbook of technical gas analysis, translation 3rd German ed., by George Lunge, 1902, p. 156.

GAS-ANALYSIS INDICATIONS.

Where the safety lamps fail to detect gas the management of a mine is ignorant regarding the actual amount of methane present in the workings, but analyses of samples taken systematically from different sections of the mine, in many returns, in the splits, in the goave, and at the face will show the exact quantity of inflammable gas present. If a split ventilating a certain part of a mine contains at any time a large amount of methane, it may be possible to force more air through that district at the expense of a less gaseous district, thereby equalizing conditions. Although the majority of mines have more air circulating through them than the law requires, often the air is not distributed to the best advantage; certain splits carrying large quantities of methane may have less air passing than other splits that have little or no methane. In some mines most of the methane in the returns is liberated in certain districts. Systematic gas analyses will accurately locate these districts. Where mine workings are extensive, individual splits may have a large territory to ventilate, and in many mines a large abandoned area, as well as the "live" workings, must be kept ventilated. So many splits may be made that the quantity of air in each approaches the minimum quantity necessary to keep the air in the territory in proper condition. It then becomes especially advantageous to determine accurately which splits carry the most methane and require the most air.

Gas analyses of mine atmospheres also serve as an aid in checking safety-lamp observations, for the analysis of a particular atmosphere examined by means of a safety lamp will show with what accuracy different men with different types of safety lamps, or with the same lamps in different conditions, or used differently, can detect fire damp. Analyses can not supplant the quick, convenient tests made with lamps, but they are an invaluable aid.

In a Bureau of Mines bulletin now in course of publication are described in detail different methods and types of apparatus used by the bureau for the chemical examination of gases. In the present paper are descriptions of those types of apparatus that are believed to be most suitable for the determination of the more common gases in coal mines, where the work usually must be performed rapidly because as a rule there is not time for the longer methods of analysis.

The value of gas analyses in connection with the fighting of mine fires is described in Technical Paper 13[a] of the bureau.

COLLECTION OF SAMPLES.

When samples are to be examined for their carbon-dioxide content they should be collected by the method of air displacement. This can be conveniently performed by attaching a small rubber pump to the sample container and forcing mine air into the container until the air that was previously in it is entirely displaced. The type of hand pump shown in figure 1 is like an ordinary syringe; it contains two valves acting against each other. Such a pump, when squeezed about 50 times, will entirely displace air from the attached 250-c. c. glass sample tube or pipette shown.

In another method of sampling one end of a rubber tube is attached to the glass pipette and the other end is held in the mouth of the operator. Eight or ten deep inhalations through the tube will completely displace the air from the pipette. Care must be exercised that the breath is exhaled away from the container because exhaled air contains about 4 per cent of carbon dioxide.

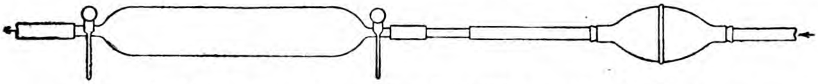

FIGURE 1.—Hand pump and container for taking samples of mine gases.

Instead of the glass pipettes with pinchcock attachments, copper or brass pipettes may be used as containers. Although their first cost is greater, they are cheaper in the long run because they are not so easily broken. They have one disadvantage, namely, that oxygen combines with the metal to a small extent, hence the proportion of oxygen determined in a sample that has been collected in them will be lower than the true proportion, depending upon the time of contact between the oxygen and the metal. Bottles with rubber stoppers secured by catches, such as are used by druggists for magnesium citrate solution, also make good gas containers. The top of a bottle should be covered with paraffin immediately after a sample is taken.

The maximum volume of sample required for the analysis, using any of the apparatus shown in this report, is 50 c. c. The use of larger containers for collecting the samples is advised so that enough of the gas will be available for several analyses. Containers having a capacity of 100 c. c. (about 3 ounces) will suffice for at least two duplicate analyses, and, in the case of the apparatus shown in figures

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[a] Burrell, G. A., and Seibert, F. M., Gas analysis as an aid in fighting mine fires. 1912. 16 pp., 1 fig.

3 and 4, for five analyses. The use of small containers is advantageous when samples are to be carried from place to place.

When samples are to be examined for methane only, they can be collected by filling the pipettes with clean water and emptying each in turn at the particular place where a sample is to be collected. Water has no appreciable solvent action upon methane.

In collecting samples of mine atmospheres, care should be exercised to have the sample represent the air current at the particular cross section selected.

The distribution of methane in the air current is not always uniform throughout the entire cross section; consequently the sample container should be moved over the area in a manner similar to that in which an anemometer is moved in taking velocity readings. When an air current is sampled, it is the practice of the Bureau of Mines to take velocity, temperature, and hygrometer readings at the same place immediately before or after the collection of the sample. The collector records also other pertinent data. The quantity of air in cubic feet passing through a particular section of a mine being known, the quantity of methane in cubic feet can be calculated from the analysis.

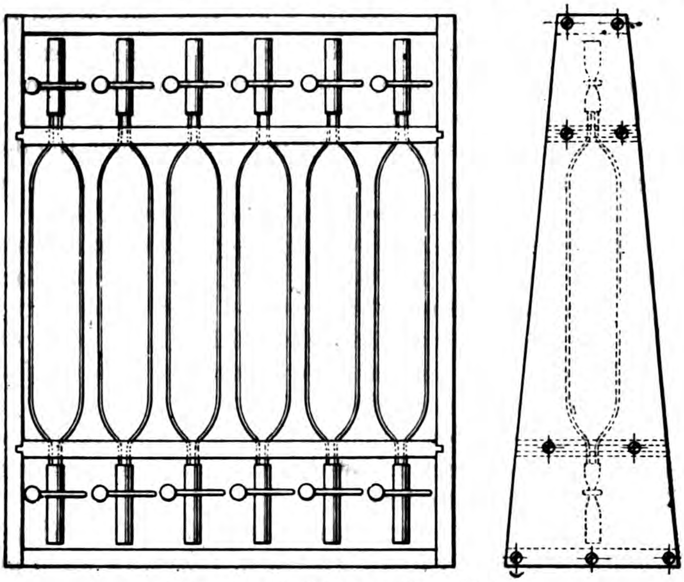

FIGURE 2.—Rack for sampling tubes.

A convenient arrangement for holding sample tubes is shown in figure 2. If 12 pipettes are desired the stand may be of similar design except for provision for a double row of pipettes. The braces holding the pipettes are removable, so that at the laboratory the pipettes can be taken out of the rack.

SAMPLING GASES TO VERIFY SAFETY-LAMP INDICATIONS.

In using gas-analysis apparatus to verify safety-lamp indications, the manner of collecting the sample is of much importance. Immediately after or before the "cap" on the safety lamp is recorded the sample container should be held close to where the air intake of the lamp was and the sample collected. The best method is for one person to take the sample while another judges the flame. It is obvious that a still accumulation of methane and air near the roof will be disturbed somewhat in handling the lamp to judge the "cap" and in collecting the sample by use of the rubber pump, so that the sample collected may not truly represent the atmosphere that entered the lamp. The best method of collecting a sample of such a pocket of methane and air is to use sample tubes from which air has been exhausted. Such a pipette as is shown in figure 1 can be exhausted at the laboratory by sealing one end of it with a blast flame and attaching the other end to a vacuum pump. A mercury gage should be connected between the pump and pipette so as to show the degree of exhaustion of the pipette. After the air has been entirely removed from the pipette, the glass tube leading to the pump can be melted off with a blast flame, thereby sealing the pipette tight. A scratch should be made on one of the tubes with a file. At the place when the sample is to be collected the scratched tube is easily broken at the file mark. It should then be sealed with a little soft wax. The Bureau of Mines uses a wax made by mixing two parts of beeswax and one part of Venice turpentine.

This method of collection is to be preferred in collecting most mine-gas samples. It is recognized, however, that a vacuum pump may not be available at many coal mines.

The next best method of collecting a sample for checking safety-lamp indications is simply to fill a bottle or tube with water and then to empty it at the place where the sample is to be collected. As previously mentioned, it should be emptied at the point where the air intake of the lamp was when the flame was observed.

APPARATUS FOR EXACT DETERMINATION OF METHANE AND CARBON DIOXIDE.

The apparatus shown in figure 3 is a modified form of the apparatus devised by Haldane,[a] but simplified for the determination of carbon dioxide and methane only. The burette has a capacity of 21 c. c., and consists of the ungraduated bulb at the top, which has a capacity of 15 c. c., and the stem which has a capacity of 6 c. c. The stem is graduated in hundredths of a cubic centimeter. To the bottom of the stem the leveling bulb *i* is attached by rubber tubing. Mercury is used as the leveling fluid. The burette can be read to 0.002 c. c., and duplicate analyses of the same sample should agree within 0.01 per

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[a] Foster, C. L. N., and Haldane, J. S., The examination of mine air, 1905, p. 36.

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cent. At *a* is the potassium hydroxide pipette for absorbing carbon dioxide, and at *b* the slow-combustion pipette for burning the methane. The potassium hydroxide solution in *a* and the mercury in *b* are of such amount that the liquids in reservoir bulbs *o* and *g* are on a line with the liquids in the corresponding pipettes.

METHOD OF USING APPARATUS.

The stopcock *c* is first turned so that communication is made between the compensating tube *e* and the outside air at *c*, thereby equalizing the pressure in the tube *e* with that of the atmosphere. Stopcock *c* is then turned so that communication is made between *e* and the column of potassium hydroxide solution in *d*. The leveling bulb *i* is raised enough to run the mercury up the burette to the stopcock *h*, thereby expelling all air from the burette. The sample container is connected to *f* by means of glass and rubber tubing. The unconnected end of the container, if a pipette, is placed in a vessel of mercury as in figure 4. If the container is a flask or bottle, it is inverted in the vessel of mercury and connection made with it in the manner indicated in figure 5. In the case of a pipette, the pinchcocks on the tubing are opened, making a clear passage from the pipette to the burette. Then, by lowering the leveling bulb *i* the mercury in the burette is brought to the 20 or the 21 c. c. mark, thereby drawing some of the sample into the burette. The stopcock *h* is closed and the mercury reservoir *i* raised a little to bring the gas in the burette under slight pressure. The sample tube is then detached from the burette at *f*, and the stopcock *h* is opened to the air for a second to bring the gas in the burette to atmospheric pressure.

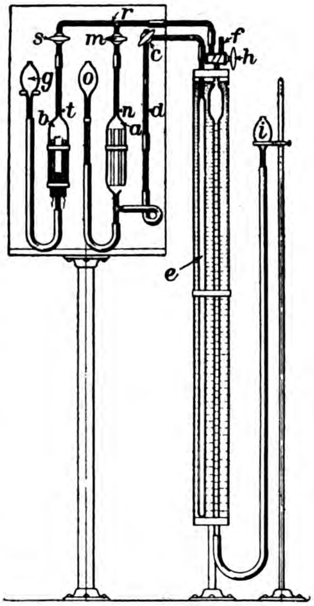

FIGURE 3.—Laboratory form of apparatus for the exact determination of carbon dioxide and methane.

The stopcocks *h* and *m* are then opened so that, through *r*, communication is made between the burette and the column of potassium hydroxide solution in *n*. By slightly raising or lowering the leveling bulb *o* the potassium-hydroxide solution is brought exactly to the mark *d*. The leveling bulb *i* is then raised or lowered until the other column of potassium hydroxide solution is brought exactly to the mark *n*. The burette is then read carefully. In this way burette readings are made against the pressure of the air in the compensating tube *e*, so that slight changes in the temperature and pressure of the outside air during the course of an analysis can be disregarded. Before a burette reading is made, the water in the water jacket should be stirred by forcing air into it through a long glass tube. A small syringe bulb like that shown in figure 1 can be used for this purpose. This precaution is necessary in order to keep the temperature of the water uniform throughout the jacket. A good method is to pass a gentle stream of compressed air continuously through the water.

The carbon dioxide is entirely removed from the sample by passing the sample back and forth several times between the burette and the potassium-hydroxide pipette *a*. The volume of gas after absorption of the carbon dioxide is determined in the same manner as was the volume of the sample, and the gas is then passed into the slow-combustion pipette *b* to burn the methane. The platinum wire is heated to a white heat and the sample is passed back and forth between the burette and the combustion pipette several times to burn completely the small amount of methane in the capillary tube *r*. In no case should the burette mercury be raised above the stopcock *h* or the mercury in the slow-combustion pipette raised to the platinum wire in burning the sample. The wire should be raised to the necessary heat slowly to avoid the danger of melting it by too strong a current. At the expiration of about two minutes the methane in the sample is completely burned.

After the pipette has cooled—cooling can be hastened by playing a stream of compressed air on the pipette—the sample is drawn back into the burette, and the contraction in volume due to combustion is measured. In returning the gas to the burette from the combustion pipette the mercury in the latter should be brought exactly to the mark *t*. This reading is taken in the same manner that the original volume of the sample was measured; that is, the stopcock *s* is closed, the stopcock *m* opened, and the solutions are adjusted in *a* and *b* as previously described. Finally, the sample is passed into the potassium hydroxide pipette *a* to absorb the carbon dioxide produced by the combustion of the methane. After the carbon dioxide has been absorbed, the reduction in volume of the gas is measured and the volume of carbon dioxide is recorded. This volume is equal to the volume of methane present in the sample and should be just one-half of the contraction produced by the combustion, as represented by the following equation:

$$CH_4+2O_2=CO_2+2H_2O$$

which shows that one volume of methane (CH_4) in burning combines with two volumes of oxygen (O_2) to form one volume of carbon dioxide (CO_2) and two volumes of gaseous water (H_2O). The gaseous water condenses immediately to liquid water and ceases to occupy appreciable space. Thus three volumes of gas enter into the reaction, whereas only one volume results. Hence the contraction produced is two-thirds the original volume of the gases, or twice the volume of the methane.

If the total volume of the original gases equaled 100 c. c., then the determined volumes of the several constituents represent the percentages of the constituents, but if the original volume was more or, as in this case, less than 100 c. c., the percentage of any one constituent is calculated by simple proportion.

The procedure outlined above does not take longer than 15 minutes.

In case methane alone is to be determined, the sample, after the first measurement in the burette, is passed directly into the slow-combustion pipette and the platinum wire is heated to incandescence. After the methane has been burned the pipette is allowed to cool and the sample is withdrawn into the burette for remeasurement. The contraction in volume due to the burning of the methane is divided by 2 and calculated to a percentage basis.

A typical tabulation of data recorded and of calculations made is given below:

Tabulation of data and calculations made.

	c. c.
Volume taken for analysis	20.000
Volume after absorption in caustic potash (potassium hydroxide) solution	19.980
Carbon dioxide in sample	.020
Volume after burning	19.900
Contraction due to burning	.080
Volume after absorption in caustic potash (potassium hydroxide) solution	19.860
Carbon dioxide produced by burning	.040

$$\text{Percentage of } CO_2 = \frac{0.02}{20.00} \times 100 = 0.10$$

$$\text{Percentage of } CH_4 = \frac{0.04}{20.00} \times 100 = 0.20$$

In using an apparatus of this type care should be taken to use heavy-wall rubber tubing for the connections and to keep the stopcocks well lubricated. A lubricant prepared by mixing pure gum rubber, vaseline, and paraffin wax is satisfactory. It is prepared as follows: 3 parts of vaseline and 1 part of paraffin are added to 1 part of melted rubber, and the mass is heated for a few minutes.

In making an analysis the potassium hydroxide solution must be kept out of the capillary tubing r; otherwise the combustion analysis for methane will be inaccurate because of carbon dioxide being absorbed by the potassium hydroxide. It is also essential that the inner walls of the burette and the compensating tube be kept slightly moistened with water. As these tubes become dry, from time to time a drop or two of water should be added. The apparatus and the mercury in it should be kept clean. Mercury can be purified by first filtering it through chamois skin or muslin and then dropping it in a fine stream through dilute nitric acid, 1 part concentrated acid (1.42 sp. gr.) to 8 parts water. Detached bubbles of potassium hydroxide solution must be kept out of the capillary tubing above *d*. In fact, all of the capillary spaces above the solutions and between the pipettes and the burette must be kept clear of liquid.

A storage battery can be used for heating the platinum wire to incandescence. One that will produce an electric current of about 4 amperes at a pressure of 5 volts is required for heating the No. 30 platinum wire. A sufficient number of dry cells, such as are used for electric doorbells or flash lights, can be used. The writers have also used some of the types of electric mine lamps on the market. The most satisfactory arrangement will result when a lamp bank or other form of resistance that will reduce the current to about 4 amperes is connected to an electric-lighting current and set up at the headquarters selected for the work, the samples being carried or mailed to this place for analysis.

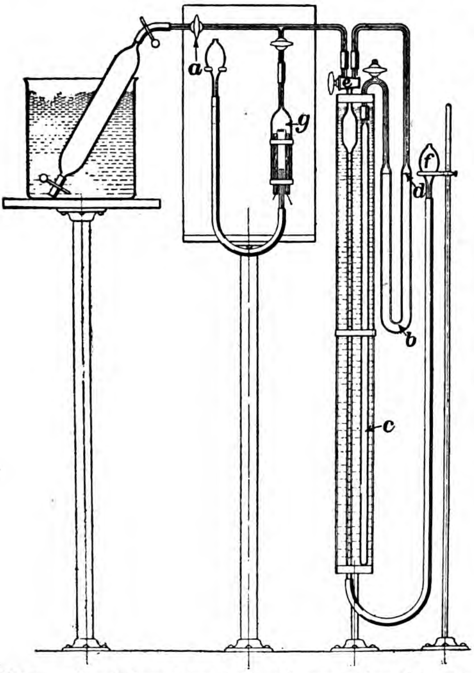

FIGURE 4.—Laboratory form of apparatus for the exact determination of methane.

APPARATUS FOR EXACT DETERMINATION OF METHANE.

The apparatus shown in figure 4 has a 21-c. c. burette similar to that used on Haldane's apparatus and the apparatus just described. The bulb has a capacity of 15 c. c. and the stem a capacity of 6 c. c. The stem is graduated in hundredths of a cubic centimeter. To the burette is attached a compensating tube that renders negligible small changes in room temperature during the course of an analysis, and thus facilitates the taking of accurate readings. The compensating device, although similar in principle to that attached to the burette of the apparatus shown in figure 3, is operated differently. The slow-combustion pipette (*g*, fig. 4) is similar in construction to that shown in figure 3.

At the laboratory the sample container is set up as shown in figure 4. About 10 c. c. of the sample is drawn into the burette and discharged through the three-way stopcock *a* to sweep out the air in the capillary tubing. About 21 c. c. of the sample is then drawn into the burette and measured against the air in the compensating tube *c* by means of the manometer *b*. The water in the manometer *b* is of such amount that at atmospheric pressure the surface of the liquid in both limbs of the U tube is approximately on a line with the scratch at *d*. After the sample has been drawn into the burette, the burette stopcock *e* is turned so that communication is made between the burette and the manometer *b*. By slightly raising or lowering the leveling bulb *f* the movement of the mercury brings the water in the U tube exactly to the mark *d*. The burette reading is then taken.

After measurement in the burette the gas is passed into the slow-combustion pipette and the platinum wire is heated. After combustion the pipette is allowed to cool and the gas is returned to the burette in order to measure the contraction in volume from the burning of the methane. This contraction divided by 2 and calculated to a percentage basis gives the proportion of methane in the sample. Duplicate determinations should agree within 0.02 per cent.

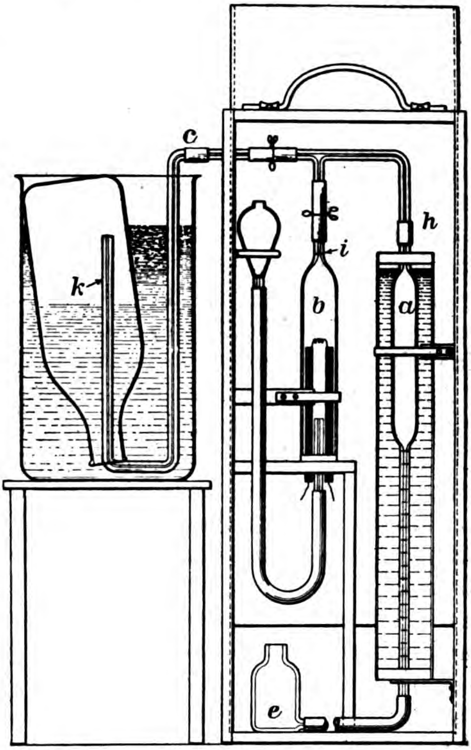

FIGURE 5.—Portable apparatus for the determination of methane.

PORTABLE APPARATUS FOR DETERMINATION OF METHANE.

Figure 5 shows a portable apparatus for the determination of methane in mine air. The burette has a capacity of 50 c. c., the capacity of the bulb being 45 c. c. and that of the stem 5 c. c. The stem is graduated in five-hundredths of a cubic centimeter. In order to simplify the apparatus, water is used instead of mercury in the burette and the combustion pipette.

With this apparatus the methane content of a sample of mine air can be determined within about 0.10 per cent. This accuracy is all that is desired in many cases. The apparatus, although not as accurate as those shown in figures 3 and 4, with which the methane can be determined with an accuracy of 0.01 per cent, possesses the advantage that it is easy to manipulate by persons who have had little or no experience in gas analysis.

To perform an analysis, the water in the combustion pipette *b* is first drawn to the mark *i* by suitable manipulation of the leveling bottle *e*. By raising this bottle water is forced out of the burette and through the tubes *k* and *h*, thereby filling all of the capillary spaces with water. The sample container is then inverted in water in the vessel, opened under water, and the tube *k* inserted in it. By opening the pinchcock on tube *c* and lowering the level bottle *e* a portion of the mine air is drawn from the sample container into the burette *a*. The surface of the water in *a* is lowered until about 48 or 50 c. c. of gas has been trapped. The pinchcock on *c* is then closed. The quantity of the sample taken is measured at atmospheric pressure by holding the level bottle *e* so that the surface of the water in it is on a line with the surface of the water in the burette.

After the sample has been measured it is forced into the slow-combustion pipette by raising *e* and opening the pinchcock above *i*. The platinum wire in the combustion pipette is then heated to a white heat, and allowed to remain so for two minutes. At the expiration of this time the methane in the sample will have been completely burned. The electric current is then broken and the pipette is allowed to cool. Cooling may be hastened by blowing air against the pipette. After the pipette has cooled, the pinchcock above *i* is opened and the sample is returned to the burette and again measured. The water in *b* is brought exactly to the mark *i*. The difference between the two readings shows the contraction in volume produced by the burning of the methane. The apparatus is contained in a carrying case which is 12 inches high, 6 inches deep, and 6 inches wide.

The results of a determination of methane in mine air, with the calculations, are given below:

Results of a determination of methane, with calculations.

	c. c.
Volume of sample taken	49. 8
Volume after burning	47. 2
Contraction due to burning	2. 6

$$\text{Volume of methane} = \frac{2.6}{2} = 1.3 \text{ c. c.}$$

$$\text{Percentage of methane} = \frac{1.3}{49.8} \times 100 = 2.6$$

For all ordinary purposes the direct reading of the contraction in cubic centimeters can be taken as the percentage of methane.

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This apparatus, as well as those shown in figures 3, 4, and 6, is intended for mixtures of methane and air that are nonexplosive—that is, contain less than 5.5 per cent methane. For mixtures richer in methane the apparatus shown in figure 7 can be used.

The percentage of methane in the workings of many coal mines is less than a device of the accuracy of that shown in figure 5 can determine, but, on the other hand, there are mines in which the proportion of methane in the main returns never falls below 0.2 to 0.5 per cent. However, the value of the apparatus shown in figure 5 lies in the fact that it can detect proportions of methane that are much below the proportion that can be detected by the safety lamp and far below the proportion that is explosive. Because of its ease of manipulation and simplicity it may appeal to officials of mines at which the employment of a chemist would not be deemed necessary.

The following results of analyses were obtained with the apparatus by a person who was not a chemist and who had never before made an analysis. The sample contained 0.33 per cent of methane.

Results of analyses with portable apparatus for determination of methane.

Determination number.	Percentage of CH_4.	Determination number.	Percentage of CH_4.
1	0.30	11	0.36
2	.30	12	.35
3	.39	13	.36
4	.30	14	.40
5	.35	15	.33
6	.26	16	.33
7	.30	17	.33
8	.24	18	.26
9	.30	19	.30
10	.40	20	.26

PORTABLE APPARATUS FOR DETERMINATION OF CARBON DIOXIDE AND METHANE.

In figure 6 is shown a portable apparatus similar to the one just described except that a caustic potash pipette (*b*) has been included for the determination of carbon dioxide. Water is used in the burette *a* and the combustion pipette *c*. The apparatus is operated in the same manner as is the one shown in figure 5, except that the sample, after measurement in the burette and before burning, is passed into the caustic potash pipette for removal of the carbon dioxide. The two determinations are accurate to about 0.10 per cent. In figure 6 *d* is the leveling bottle for the burette and *e* the leveling bulb for the slow-combustion pipette. Connection with the sample container is made at *f*.

The percentages of carbon dioxide in a given sample (actual carbon-dioxide content, 0.73 per cent), as determined by a series of six analyses with the apparatus, were as follows: 0.82, 0.71, 0.71, 0.90, 0.90, 0.91; the percentages determined in two analyses of another sample actually containing 0.28 per cent carbon dioxide were 0.40 and 0.30.

MODIFIED ORSAT APPARATUS FOR COMPLETE APPROXIMATE ANALYSIS OF MINE AIR.

The portable apparatus shown in figure 7 consists essentially of the burette *e* and the four pipettes *a*, *b*, *c*, and *d*. The burette has a capacity of 50 cubic centimeters and is graduated to two-tenths of one cubic centimeter. The case is 12 inches high, 6½ inches wide, and 6 inches deep. Pipette *a* contains potassium hydroxide solution for the removal of carbon dioxide, pipette *b* contains alkaline pyrogallate solution for the removal of oxygen, pipette *c* contains ammoniacal cuprous chloride solution for the removal of carbon monoxide, and pipette *d* is the slow-combustion pipette for burning the methane in the sample of mine air. Pipettes *a*, *b*, and *c* contain glass rods (not shown) to increase the absorbent surface of the reagents. The platinum wire inside the combustion pipette is No. 30 (B. & S. gage), and is supported by two hollow glass rods. It is sealed to copper wires that pass down through the rods. The lower ends of the copper wires may be connected to a storage battery, or other source of electric current. The combustion pipette is filled with distilled water slightly acidified with sulphuric acid. At *f* and *g* are leveling bottles.

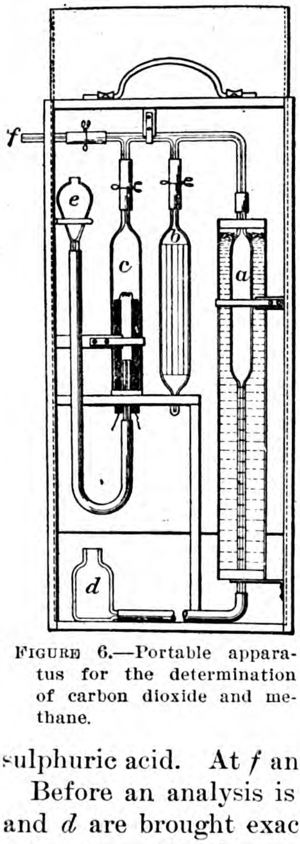

FIGURE 6.—Portable apparatus for the determination of carbon dioxide and methane.

Before an analysis is begun the solutions in the pipettes *a*, *b*, *c*, and *d* are brought exactly to the marks indicated on the capillary tubes above the pipettes by suitable manipulation of the level bottle *f*. The stopcocks are then closed as shown in the figure. In order to draw a sample of gas into the burette *e*, the water therein is raised to the point *h* by raising *f*, opening the stopcock *i* to the air, and finally, when the water is at *h*, by again closing *i*. A rubber connection is made between *i* and the sample container, and the container is placed in a vessel of water. All connections are then opened, including the stopcocks or pinchcocks on the sample container and the stopcock *i*, and the level bottle *g* is lowered until the water in the burette *e* is brought approximately to the lowest division on the burette.

The first few cubic centimeters of a sample is used to sweep air from the connecting tubes. The stopcock *i* is then closed to the outside air and the gas sample in the burette is measured at atmospheric pressure by holding the level bottle *g* in such a position that the surface of the water in it is on a line with the surface of the water in the burette. One minute is allowed, after the sample has been brought into the burette, before the measurement is taken, in order to guard against a small error that would result if this short interval of time were not allowed for drainage of water down the sides of the burette.

After measurement the sample is passed into the potassium hydroxide pipette *a* and the carbon dioxide is removed by passing the sample three or four times back and forth between the pipette and the burette. Finally the solution in the pipette *a* is brought exactly to the mark on the capillary stem and the sample is measured, one minute's time for drainage being again allowed. The loss in volume shows the amount of carbon dioxide originally present in the gas sample.

The sample is next passed into the pipette *b* to remove the oxygen, and manipulations are made in the same manner as for the removal of carbon dioxide. However, an alkaline pyrogallate solution does not remove oxygen from a gas mixture as rapidly as a caustic potash solution removes carbon dioxide from a mixture; consequently more time for contact between this solution and the sample must be allowed. Five or six passages are usually sufficient even with an alkaline pyrogallate solution that has been used a number of times.

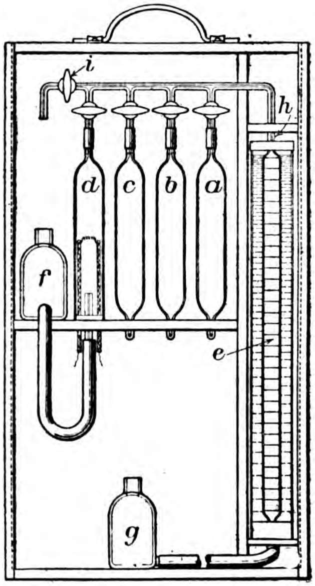

FIGURE 7.—Modified Orsat apparatus for the complete analysis of mine air.

After the sample has been measured in the burette and the contraction in volume, due to the absorption of oxygen, has been recorded, the sample is passed into the pipette *c* for the removal of carbon monoxide. Cuprous chloride is less satisfactory as an absorbent than is an alkaline pyrogallate solution, especially if the cuprous chloride solution be confined in an Orsat pipette, and the absorption be conducted under the conditions mentioned. In fact, when the carbon monoxide amounts to more than 1 per cent of the total volume of the sample, absorption is scarcely complete even after prolonged contact, especially if the solution has been used several times previously for absorbing carbon monoxide. However, more than 1 per cent of carbon monoxide is seldom found in mine atmosphere that may be sampled, even shortly after mine fires or explosions.

Absorption of the gas in any pipette may usually be considered complete if no difference in the volume of the sample is observed by two successive passages of the sample into the pipette and measurement in the burette.

The caustic potash solution in the pipette *a* may be used for many analyses, because a caustic potash solution has a large capacity for absorbing carbon dioxide. The alkaline pyrogallate solution is less active; consequently its efficiency must be verified occasionally by using the apparatus to determine the oxygen in outside air. The proportion of oxygen found with the apparatus shown should be 20.8 to 21.1 per cent. The proportion of oxygen in pure, dry, outside air is 20.93 per cent. Unavoidable sources of error in the use of the Orsat apparatus account for a possible variation of about 0.1 per cent or even 0.2 per cent from the true figures.

Attention is called to the fact that if carbon dioxide is not removed by the caustic potash solution, it will be absorbed by the alkaline pyrogallate solution, and if the latter solution does not entirely remove the oxygen some of it will be absorbed by the cuprous chloride solution. Hence, it is absolutely necessary to make sure that the absorption of gas in a given pipette is complete before the residual gas is passed to the next pipette.

After the constituents absorbable by the reagents are removed, the sample, if it contains less than an explosive proportion of methane, is diluted with air or oxygen by lowering the level bottle *g* (fig. 7), opening the stopcock *i* to the outside air, and drawing some of the air into the burette, so that the combined volume of air and residual gas amounts to 48 or 50 c. c. After measurement the sample is passed into the slow-combustion pipette *d*. The platinum wire therein is heated to a white heat for two minutes. After the pipette *d* has become cool to the hand the residual gas is drawn into the burette and the contraction in volume due to the burning of the methane is determined. The gas is then passed into the pipette *a*, and the carbon dioxide produced by the burning of the methane is absorbed by the caustic potash solution. The residue is then returned to the burette and the contraction in volume due to the absorption of carbon dioxide is recorded. The carbon dioxide produced by the burning of the methane should be equal to one-half of the contraction. If this relation does not hold good within 0.2 c. c., some other combustible gas than methane is present, or an error has been made in the manipulation.

If the proportion of methane in the sample is too large to be determined by the method of dilution, as described above, the gas left after the absorbable constituents have been removed may be passed directly into the slow-combustion pipette. The platinum wire is then heated and oxygen is slowly passed into the pipette. The methane burns as fast as the oxygen enters and an explosion can not follow. The rest of the analysis is performed in the manner already described. A final determination of oxygen should be made to determine that sufficient oxygen was present to burn the methane completely.

A specimen tabulation of the analysis results and the calculations recorded in the analysis of the mine-gas mixture containing CO_2, O_2, CO, CH_4, H_2, and N_2 is given below:

Sample record of results of analysis of a mine-gas mixture.

	c. c.
Volume taken for analysis	50.0
Volume after caustic potash absorption	48.7
CO_2 in sample	1.3
Volume after alkaline pyrogallate absorption	40.8
Oxygen in sample	7.9
Volume after cuprous chloride absorption	40.4
CO in sample	.4
Volume taken for combustion	40.4
Oxygen added	9.0
Total volume	49.4
Volume after combustion	45.3
Contraction due to combustion	4.1
Volume after caustic potash absorption	43.4
CO_2 produced by combustion (methane)	1.9

$$\text{Hydrogen}=\frac{2}{3}\,[4.1-2\,(1.9)]=0.2 \text{ c. c.}$$

Results of analysis.

	Per cent.
CO_2	2.6
O_2	15.8
CO	.8
CH_4	3.8
H_2	.4
N_2 (by difference)	76.6

When carefully conducted such an analysis should not vary more than 0.20 or 0.25 per cent from the truth. Frequently the accuracy is greater than this, and is almost invariably in the case of the absorbable constituents of a gas mixture.

PREPARATION OF SOLUTIONS—DETAILS OF APPARATUS.

The solutions mentioned in connection with the apparatus herein described are prepared as described below:

CAUSTIC POTASH SOLUTION.

Three hundred and thirty grams of caustic potash, chemically pure, stick form, is dissolved in 1,000 c. c. of distilled water.

ALKALINE PYROGALLATE SOLUTION.[a]

Five grams of pyrogallic acid is dissolved in 15 c. c. of distilled water; 120 grams of caustic potash, chemically pure, stick form, is dissolved in 80 c. c. of distilled water. For use the two solutions are mixed together in the alkaline pyrogallate pipette. Care should be taken not to expose the solution to the air.

CUPROUS CHLORIDE SOLUTION.[b]

Two hundred and fifty grams of ammonium chloride and 200 grams of cuprous chloride are dissolved in 750 c. c. of distilled water. Copper foil or wire should be placed in this stock solution. For use the solution is mixed with one-third its volume of ammonia water, specific gravity 0.90.

APPARATUS REQUIRED.

The laboratory apparatus necessary for the analysis of mine gases by means of the apparatus shown at figure 7 includes the following items:

Laboratory apparatus necessary for analyzing mine gases.

1. 1 nest of beakers, Nos. 0 to 6, inclusive.
2. 1 graduated cylinder, capacity 500 c. c.
3. 1 pair of scales, capacity 1 kilogram, sensitive to 0.1 gram.
4. 1 set of weights, 1 gram to 500 grams.
5. 1 spatula.
6. 10 feet of black rubber tubing, heavy wall, internal diameter 5 mm.
7. 10 feet of white rubber tubing, light wall, internal diameter 7 mm.
8. 2 pounds of assorted glass tubing.
9. 1 pound of capillary glass tubing, 1 mm. internal diameter.
10. 6 pinchcocks, Mohr's, medium size.
11. 6 screw clamps, Chapman's, medium size.
12. 3 feet of platinum wire, No. 30 (B. & S.) gage.
13. 12 sampling tubes or bottles, each about 200 c. c. capacity, fitted with pinchcocks or stopcocks.
14. 1 spool of copper wire, No. 18 (B. & S.) gage.
15. 6 reagent bottles, three 1,000-c. c. and three 500-c. c.

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[a] Hempel, Walther, Methods of gas analysis. Engl. trans. by L. M. Dennis, 1910, p. 149.

[b] Winkler, Clemens, Handbook of technical gas analysis. 2d ed. of Engl. trans. by George Lunge, 1902, p. 73.

If the electric current at the mine has a pressure of 220 volts, ten 32-c. p. or twenty 16-c. p. lamps connected in parallel will be required to produce a current strength of 5 amperes. If the pressure is 110 volts, ten 16-c. p. lamps will be required. If the pressure is 55 volts, five 16-c. p. lamps will be required. A wire-wound resistance box can also be used.

For the preparation of reagents the following supplies will be required:

Supplies necessary for preparing reagents.

16. 5 pounds of potassium hydroxide.
17. 5 pounds of cuprous chloride.
18. 5 pounds of ammonium chloride.
19. 1 pound of pyrogallic acid.
20. 6 pounds of ammonia water.
21. Distilled or good, potable water.

If an apparatus for the determination of methane and carbon dioxide is procured, items 1 to 16, inclusive, and item 21 should be obtained. In the case of a methane apparatus item 6 and items 8 to 14, inclusive, should be obtained.

All of the apparatus shown in this report are only modifications of existing types long used by gas analysts, the modifications being made to suit the conditions existing at coal mines.

The compensating device of the apparatus shown in figure 3 is similar to that used by Haldane. That attached to the apparatus shown in figure 4 is similar to the type used by Hempel,[a] although both depend upon the principle of Pettersson,[b] who was the first to show that, by means of a tube inclosing a volume of gas, errors resulting from variations in the pressure and temperature of the atmosphere at the time of an analysis can be compensated for.

The construction of the slow-combustion pipettes follows Winkler's[c] design as modified for use with mercury by that of Dennis, although the use of a platinum wire for burning combustible gases originated with Coquillon.[d]

The ordinary Orsat apparatus widely used for flue-gas analysis is well known. A slow-combustion pipette was included for burning combustible gases, and the burette was made of the same diameter from top to bottom, so it could be read at any point.

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[a] Hempel, Walther, Methods of gas analysis, Engl. trans. by L. M. Dennis, 1910, p. 61.

[b] Zeitsch. anal. Chemie, vol. 25, pp. 467, 484.

[c] Winkler, Clemens, Handbook of technical gas analysis, Engl. trans. by George Lunge, 1902, p. 152.

[d] Compt. Rend., vol. 84, 1877, p. 458.

PUBLICATIONS ON MINE ACCIDENTS AND METHODS OF MINING.

The following Bureau of Mines publications may be obtained free by applying to the Director, Bureau of Mines, Washington, D. C.

BULLETIN 10. The use of permissible explosives, by J. J. Rutledge and Clarence Hall. 1912. 34 pp., 5 pls., 4 figs.

BULLETIN 17. A primer on explosives for coal miners, by C. E. Munroe and Clarence Hall. 61 pp., 10 pls., 12 figs. Reprint of United States Geological Survey Bulletin 423.

BULLETIN 20. The explosibility of coal dust, by G. S. Rice, with chapters by J. C. W. Frazer, Axel Larsen, Frank Haas, and Carl Scholz. 204 pp., 14 pls., 28 figs. Reprint of United States Geological Survey Bulletin 425.

BULLETIN 44. First national mine-safety demonstration, Pittsburgh, Pa., October 30 and 31, 1911, by H. M. Wilson and A. H. Fay, with a chapter on the explosion at the experimental mine by G. S. Rice. 1912. 75 pp., 7 pls., 4 figs.

BULLETIN 45. Sand available for filling mine workings in the Northern Anthracite Coal Basin of Pennsylvania, by N. H. Darton. 1913. 33 pp., 8 pls., 5 figs.

BULLETIN 46. An investigation of explosion-proof mine motors, by H. H. Clark. 1912. 44 pp., 6 pls., 14 figs.

BULLETIN 52. Ignition of mine gases by the filaments of incandescent electric lamps, by H. H. Clark and L. S. Ilsley. 1913. 31 pp., 6 pls., 2 figs.

TECHNICAL PAPER 11. The use of mice and birds for detecting carbon monoxide after mine fires and explosions, by G. A. Burrell. 1912. 15 pp.

TECHNICAL PAPER 13. Gas analysis as an aid in fighting mine fires, by G. A. Burrell and F. M. Seibert. 1912. 16 pp., 1 fig.

TECHNICAL PAPER 19. The factor of safety in mine electrical installations, by H. H. Clark. 1912. 14 pp.

TECHNICAL PAPER 21. The prevention of mine explosions; report and recommendations, by Victor Watteyne, Carl Meissner, and Arthur Desborough. 12 pp. Reprint of United States Geological Survey Bulletin 369.

TECHNICAL PAPER 22. Electrical symbols for mine maps, by H. H. Clark. 1912. 11 pp., 8 figs.

TECHNICAL PAPER 24. Mine fires; a preliminary study, by G. S. Rice. 1912. 51 pp., 1 fig.

TECHNICAL PAPER 28. Ignition of mine gas by standard incandescent lamps, by H. H. Clark. 1912. 6 pp.

TECHNICAL PAPER 29. Training with mine-rescue breathing apparatus, by J. W. Paul. 1912. 16 pp.

MINERS' CIRCULAR 3. Coal-dust explosions, by G. S. Rice. 1911. 22 pp.

MINERS' CIRCULAR 4. The use and care of mine-rescue breathing apparatus, by J. W. Paul. 1911. 24 pp., 5 figs.

MINERS' CIRCULAR 5. Electrical accidents in mines; their causes and prevention, by H. H. Clark, W. D. Roberts, L. C. Ilsley, and H. F. Randolph. 1911. 10 pp., 3 pls.

MINERS' CIRCULAR 6. Permissible explosives tested prior to January 1, 1912, and precautions to be taken in their use, by Clarence Hall. 1912. 20 pp.

MINERS' CIRCULAR 9. Accidents from falls of roof and coal, by G. S. Rice. 1912. 16 pp.

MINERS' CIRCULAR 10. Mine fires and how to fight them, by J. W. Paul. 1912. 14 pp.

MINERS' CIRCULAR 11. Accidents from mine cars and locomotives, by L. M. Jones. 1912. 16 pp.

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